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# Hyperfine structure of alkali-metal diatomic molecules

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We present calculations of the hyperfine coupling constants for all the heteronuclear alkali-metal diatomic molecules at the equilibrium geometry of the electronic ground state. These constants are important in developing methods to control ultracold polar molecules. The results are based on electronic structure calculations using density-functional theory, and are in good agreement with experiment for the limited set of molecules for which experiments are so far available.

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## I. INTRODUCTION

It has recently become possible to produce samples of ultracold polar molecules at temperatures around 1  $\mu$ K, by combining pairs of ultracold alkali-metal atoms by magnetoassociation and then transferring them to their rovibronic ground state by stimulated Raman adiabatic passage. The polar molecules produced so far include  $^{40}\text{K}^{87}\text{Rb}$  [1],  $^{87}\text{Rb}^{133}\text{Cs}$  [2,3],  $^{23}\text{Na}^{40}\text{K}$  [4], and  $^{23}\text{Na}^{87}\text{Rb}$  [5]. Such molecules have many potential applications, ranging from quantum-state-controlled chemistry [6–9] to quantum simulation [10,11] and quantum information [12,13].

All the stable isotopes of the alkali metals have nonzero nuclear spin. In the diatomic molecules, the two spins interact with one another and with the molecular rotation to form complex patterns of energy levels. These energy levels cross and avoided-cross as a function of magnetic and electric fields [14–16] and laser intensity [17]. Understanding the energy levels and their crossings is crucial in developing schemes to control ultracold molecules and transfer them between rotational and hyperfine states.

We have previously carried out calculations of the hyperfine coupling constants of KRb and RbCs [14] and LiCs [16], using density-functional theory (DFT). The purpose of the present paper is to extend these calculations to the full set of heteronuclear diatomic molecules formed from alkali-metal atoms. We compare the results with experiments [7,18,19] where possible.

## II. MOLECULAR HAMILTONIAN

The effective Hamiltonian of a  $^1\Sigma$  diatomic molecule, with hyperfine structure, in the presence of external magnetic and electric fields may be written [14,17,20–22]

$$H = H_{\text{rot}} + H_{\text{hf}} + H_{\text{S}} + H_{\text{Z}}, \quad (1)$$

where  $H_{\text{rot}}$ ,  $H_{\text{hf}}$ ,  $H_{\text{S}}$ , and  $H_{\text{Z}}$  are rotational, hyperfine, Stark, and Zeeman terms:

$$H_{\text{rot}} = B_v N^2 - D_v N^2 \cdot N^2, \quad (2)$$

$$H_{\text{hf}} = \sum_{i=1}^2 \mathbf{V}_i : \mathbf{Q}_i + \sum_{i=1}^2 c_i \mathbf{N} \cdot \mathbf{I}_i + c_3 \mathbf{I}_1 \cdot \mathbf{T} \cdot \mathbf{I}_2 + c_4 \mathbf{I}_1 \cdot \mathbf{I}_2, \quad (3)$$

$$H_{\text{S}} = -\boldsymbol{\mu} \cdot \mathbf{E} - \frac{1}{2} \mathbf{E} \cdot \boldsymbol{\alpha} \cdot \mathbf{E}, \quad (4)$$

$$H_{\text{Z}} = -g_{\text{r}} \mu_{\text{N}} \mathbf{N} \cdot \mathbf{B} - \sum_{i=1}^2 g_i \mu_{\text{N}} \mathbf{I}_i \cdot \mathbf{B} (1 - \sigma_i). \quad (5)$$

Here  $\mathbf{I}_1$  and  $\mathbf{I}_2$  are the spins of nuclei 1 and 2 and  $\mathbf{N}$  is the angular momentum for rotation of the molecule about its center of mass. The rotational and centrifugal distortion constants of the molecule are  $B_v$  and  $D_v$ , though centrifugal distortion is neglected below. The hyperfine Hamiltonian (3) consists of four terms. The first is the interaction between the nuclear electric quadrupole tensor  $\mathbf{Q}$  and the electric-field gradient  $\mathbf{V}$  due to the electrons, which is characterized by coupling constants  $(eQq)_1$  and  $(eQq)_2$ . The second is the interaction between the nuclear magnetic moments and the magnetic field created by the rotation of the molecule, with spin-rotation coupling constants  $c_1$  and  $c_2$ . The final two terms are the tensor and scalar interactions between the nuclear dipole moments, with spin-spin coupling constants  $c_3$  and  $c_4$ , respectively.

The Stark Hamiltonian (4) includes both a linear term to describe the interaction of the molecular dipole  $\boldsymbol{\mu}$  with a static electric field  $\mathbf{E}$  and a quadratic term involving the molecular polarizability tensor  $\boldsymbol{\alpha}$ . The latter is usually small for static fields, but may be used with a frequency-dependent polarizability  $\boldsymbol{\alpha}(\omega)$  to account for the ac Stark effect due to a nonresonant laser field [17]. The Zeeman Hamiltonian (5) describes the interaction of the molecule with an external magnetic field  $\mathbf{B}$ , and consists of two terms representing the rotational and nuclear Zeeman effects. In the latter,  $g_i$  and  $\sigma_i$  are the nuclear  $g$  factor and the shielding factor for nucleus  $i$ .

## III. EVALUATION OF THE COUPLING CONSTANTS

In the present paper we evaluate the hyperfine coupling constants from electronic structure calculations using DFT. The methods used are the same as in Ref. [14], and so will be summarized only briefly here. The calculations are performed with

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TABLE I. Nuclear properties and rotational and hyperfine coupling constants for the heteronuclear alkali-metal diatomic molecules. Indices 1 and 2 refer to the first and second atom, respectively. Calculations were performed as described in the text.

	$I_1$	$I_2$	$g_1$	$g_2$	$(eQq)_1(\text{MHz})$	$(eQq)_2(\text{MHz})$	$\sigma_1(\text{ppm})$	$\sigma_2(\text{ppm})$	$c_1(\text{Hz})$	$c_2(\text{Hz})$	$c_3(\text{Hz})$	$c_4(\text{Hz})$
$^6\text{Li } ^{23}\text{Na}$	1	3/2	0.822	1.478	$8 \times 10^{-4}$	-0.684	102.3	613.6	84.0	805.3	196.6	212.2
$^7\text{Li } ^{23}\text{Na}$	3/2	3/2	2.171	1.478	0.038	-0.684	102.3	613.6	196.9	714.2	519.2	560.4
$^6\text{Li } ^{39}\text{K}$	1	3/2	0.822	0.261	$4 \times 10^{-4}$	-0.854	104.1	1296.8	48.3	238.8	23.1	58.7
$^6\text{Li } ^{40}\text{K}$	1	4	0.822	-0.324	$4 \times 10^{-4}$	1.066	104.1	1296.8	48.2	-295.5	-28.7	-72.8
$^6\text{Li } ^{41}\text{K}$	1	3/2	0.822	0.143	$4 \times 10^{-4}$	-1.038	104.1	1296.8	48.0	130.0	12.6	32.1
$^7\text{Li } ^{39}\text{K}$	3/2	3/2	2.171	0.261	0.021	-0.854	104.1	1296.8	111.9	209.3	61.0	155.0
$^7\text{Li } ^{40}\text{K}$	3/2	4	2.171	-0.324	0.021	1.066	104.1	1296.8	111.5	-258.9	-75.7	-192.4
$^7\text{Li } ^{41}\text{K}$	3/2	3/2	2.171	0.143	0.021	-1.038	104.1	1296.8	111.1	113.8	33.4	84.9
$^6\text{Li } ^{85}\text{Rb}$	1	5/2	0.822	0.541	$2 \times 10^{-4}$	-7.774	105.4	3419.8	36.0	1177.0	44.7	261.4
$^6\text{Li } ^{87}\text{Rb}$	1	3/2	0.822	1.834	$2 \times 10^{-4}$	-3.760	105.4	3419.8	36.0	3983.8	151.7	886.3
$^7\text{Li } ^{85}\text{Rb}$	3/2	5/2	2.171	0.541	0.012	-7.774	105.4	3419.8	82.5	1020.2	118.1	690.5
$^7\text{Li } ^{87}\text{Rb}$	3/2	3/2	2.171	1.834	0.012	-3.760	105.4	3419.8	82.3	3452.3	400.7	2340.9
$^6\text{Li } ^{133}\text{Cs}$	1	7/2	0.822	0.738	$3 \times 10^{-4}$	0.181	108.0	6244.0	15.2	3475.5	53.1	620.8
$^7\text{Li } ^{133}\text{Cs}$	3/2	7/2	2.171	0.738	0.017	0.181	108.0	6244.0	34.7	3001.2	140.1	1639.7
$^{23}\text{Na } ^{39}\text{K}$	3/2	3/2	1.478	0.261	-0.133	-0.613	624.4	1297.4	118.5	78.9	39.0	362.5
$^{23}\text{Na } ^{40}\text{K}$	3/2	4	1.478	-0.324	-0.133	0.765	624.4	1297.4	117.4	-97.0	-48.4	-450.0
$^{23}\text{Na } ^{41}\text{K}$	3/2	3/2	1.478	0.143	-0.133	-0.745	624.4	1297.4	116.4	42.4	21.4	198.6
$^{23}\text{Na } ^{85}\text{Rb}$	3/2	5/2	1.478	0.541	-0.132	-6.170	629.6	3437.6	61.0	291.6	76.5	1690.3
$^{23}\text{Na } ^{87}\text{Rb}$	3/2	3/2	1.478	1.834	-0.132	-2.984	629.6	3437.6	60.7	983.8	259.3	5730.3
$^{23}\text{Na } ^{133}\text{Cs}$	3/2	7/2	1.478	0.738	-0.097	0.150	639.2	6278.7	14.2	854.5	105.6	3941.8
$^{39}\text{K } ^{85}\text{Rb}$	3/2	5/2	0.261	0.541	-0.249	-3.066	1321.0	3469.0	19.9	126.8	11.5	482.1
$^{39}\text{K } ^{87}\text{Rb}$	3/2	3/2	0.261	1.834	-0.249	-1.483	1321.0	3469.0	19.8	426.9	38.8	1634.3
$^{40}\text{K } ^{85}\text{Rb}$	4	5/2	-0.324	0.541	0.311	-3.066	1321.0	3469.0	-24.3	124.7	-14.2	-598.5
$^{40}\text{K } ^{87}\text{Rb}$	4	3/2	-0.324	1.834	0.311	-1.483	1321.0	3469.0	-24.1	419.5	-48.2	-2028.8
$^{41}\text{K } ^{85}\text{Rb}$	3/2	5/2	0.143	0.541	-0.303	-3.066	1321.0	3469.0	10.5	122.6	6.3	264.1
$^{41}\text{K } ^{87}\text{Rb}$	3/2	3/2	0.143	1.834	-0.303	-1.483	1321.0	3469.0	10.5	412.5	21.3	895.4
$^{39}\text{K } ^{133}\text{Cs}$	3/2	7/2	0.261	0.738	-0.182	0.075	1340.7	6337.1	8.6	385.4	18.0	1146.3
$^{40}\text{K } ^{133}\text{Cs}$	4	7/2	-0.324	0.738	0.227	0.075	1340.7	6337.1	-10.5	377.9	-22.3	-1422.9
$^{41}\text{K } ^{133}\text{Cs}$	3/2	7/2	0.143	0.738	-0.221	0.075	1340.7	6337.1	4.5	370.8	9.9	628.0
$^{85}\text{Rb } ^{133}\text{Cs}$	5/2	7/2	0.541	0.738	-1.611	0.054	3531.6	6367.3	29.2	196.5	56.8	5116.7
$^{87}\text{Rb } ^{133}\text{Cs}$	3/2	7/2	1.834	0.738	-0.779	0.054	3531.6	6367.3	97.6	193.7	192.5	17345.8

the Amsterdam Density Functional (ADF) package [23,24]. We employ all-electron QZ4P basis sets (quadruple- $\zeta$  basis sets with four polarization functions). Relativistic corrections are included by means of the two-component zeroth-order regular approximation [25–27], including spin-orbit coupling as well as scalar effects. We use different density functionals for different properties: quadrupole coupling constants are obtained from calculations with the B3LYP functional [28,29], while spin-spin coupling constants are obtained with the Perdew-Burke-Ernzerhof functional [30]. Shielding tensors and the related spin-rotation constants are evaluated using the KT2 functional [31]. All these choices are justified in Ref. [14].

ADF generally calculates hyperfine coupling constants for the most common isotope of each element. In the present paper we provide values for all combinations of stable isotopes by performing simple scalings according to nuclear  $g$  factors, nuclear quadrupole moments [32,33], and molecular rotational constants. The results obtained are given in Table I.<sup>1</sup> The

calculations were performed at the equilibrium geometry for each molecule,  $R_e = 2.88 \text{ \AA}$  for LiNa [34],  $3.32 \text{ \AA}$  for LiK [35],  $3.43 \text{ \AA}$  for LiRb [36],  $3.67 \text{ \AA}$  for LiCs [37],  $3.45 \text{ \AA}$  for NaK [38],  $3.64 \text{ \AA}$  for NaRb [39],  $3.85 \text{ \AA}$  for NaCs [40],  $4.07 \text{ \AA}$  for KRb [41],  $4.28 \text{ \AA}$  for KCs [42], and  $4.37 \text{ \AA}$  for RbCs [43]. The values of the permanent dipole moments, not included in Table I, can be found in Ref. [44].

#### IV. COMPARISON WITH EXPERIMENT

Experimental determinations of the hyperfine coupling constants from molecular spectroscopy are mostly limited to the scalar spin-spin coupling constant  $c_4$  and the nuclear quadrupole coupling constants  $(eQq)_1$  and  $(eQq)_2$ . In particular, the ground rotational state ( $N = 0$ ) is almost unaffected by any hyperfine couplings except  $c_4$  [14]. At zero magnetic field it splits into  $2I_{\min} + 1$  states, where  $I_{\min}$  is the smaller of  $I_1$  and  $I_2$ . These correspond to the different possible values of the total angular momentum  $F$ , which for  $N = 0$  is the same

<sup>1</sup>Values for  $^7\text{Li } ^{133}\text{Cs}$ , KRb, and RbCs, obtained with similar methods, were presented previously [14,16]. The values in Table I differ slightly (by around 1% except for some values of  $eQq$ )

because we used tighter DFT convergence criteria and updated nuclear quadrupoles [33] in the present paper.

TABLE II. Comparison between experimental and theoretical values of molecular constants. Indices 1 and 2 refer to the first and second atom, respectively.

	$(eQq)_1(\text{MHz})$	$(eQq)_2(\text{MHz})$	$c_4(\text{Hz})$	Reference
$^{40}\text{K } ^{87}\text{Rb}$	0.45(6)	-1.41(4)		[7]
	0.311	-1.483		This paper and [14]
$^{23}\text{Na } ^{40}\text{K}$	-0.187(35)	0.899(20)	-409(10)	[18]
	-0.133	0.765	-450.0	This paper
$^{87}\text{Rb } ^{133}\text{Cs}$	-0.80929(113)	0.05998(186)	19019(105)	[19]
	-0.779	0.054	17345.8	This paper and [14]

as the total nuclear spin  $I$ . The splitting between the highest and lowest states due to the hyperfine coupling is

$$\Delta E_{N=0}^{\text{hf}} = \frac{|c_4|}{2} [(I_1 + I_2)(I_1 + I_2 + 1) - |I_1 - I_2|(|I_1 - I_2| + 1)] \quad (6)$$

and ranges from 1.3 kHz for  $^6\text{Li } ^{41}\text{K}$  to 208 kHz for  $^{87}\text{Rb } ^{133}\text{Cs}$ .

For  $N > 0$  the hyperfine splitting is more complicated and is commonly dominated by the nuclear electric quadrupole interaction, with a minor contribution from the scalar spin-spin interaction. Under these circumstances, the splitting between the highest and lowest  $N = 1$  levels,  $\Delta E_{N=1}^{\text{hf}}$ , is approximately half the larger of the two nuclear electric quadrupole coupling constants. This can be as much as 4 MHz for  $^6\text{Li } ^{85}\text{Rb}$  and  $^7\text{Li } ^{85}\text{Rb}$ . For some molecules such as  $^{23}\text{Na } ^{133}\text{Cs}$  or  $^7\text{Li } ^{133}\text{Cs}$ , however, the nuclear electric quadrupole interactions are small enough (tens of kilohertz) to be comparable to the scalar spin-spin interaction, and the two effects influence the hyperfine splittings by similar amounts. The tensorial spin-spin and spin-rotation interactions play a minor role for low- $N$  states, though the spin-rotation interaction may become significant for experiments involving higher rotational levels.

Table II compares the calculated hyperfine constants to experimental values where available. The calculated values

are mostly within 10% of experiment, and always within 20%, except for  $(eQq)_{\text{Na}}$  in  $^{23}\text{Na } ^{40}\text{K}$  and  $(eQq)_{\text{K}}$  in  $^{40}\text{K } ^{87}\text{Rb}$ , which are experimentally less well determined than most other constants.

## V. CONCLUSIONS

We have presented calculations of the hyperfine coupling constants for all heteronuclear alkali-metal diatomic molecules formed from stable isotopes, using electronic structure calculations based on density-functional theory. Characterizing the hyperfine structure of these molecules is essential to controlling them and developing their applications in ultracold quantum physics. Our results are in good agreement with the (still scarce) experimental measurements of these molecular properties.

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